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The Synthesis and *Ab Initio* Structure Determination of $Zn_4O(BO_3)_2$, a Microporous Zincoborate Built Up from "Fused" 3-Ring and 5-Ring Sub-units**

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## ABSTRACT

The synthesis and structure of $Zn_4O(BO_3)_2$, a new, neutral-framework, microporous zincoborate are reported. The crystal structure of $Zn_4O(BO_3)_2$ has been solved *ab initio* from laboratory X-ray powder diffraction data, and consists of a network of vertex-sharing tetrahedral $ZnO_4$ and triangular $BO_3$ moieties enclosing interlinked, "cigar"-shaped cages and a three-dimensional network of intersecting channels (minimum diameter ~3.5 Å). The "fused" 3-ring/5-ring connectivity of the Zn/B/O framework is novel. Crystal data: $Zn_4O(BO_3)_2$, $M_r = 384.37$, rhombohedral, space group $R\bar{3}c$ (No. 167), $a = 9.9115\,(4)$ Å, $\alpha = 48.602\,(1)^\circ$, $V = 502.61$ Å$^3$, $Z = 3$, $R_p = 10.9\%$, $R_{wp} = 14.2\%$ for 4198 powder data (Cu K$\bar{\alpha}$ radiation, $\lambda = 1.54178$ Å).

## Short Text for Table of Contents

The syntheses, structures and properties of non-aluminosilicate molecular sieves are currently of great interest. Most previous studies have concentrated on tetrahedrally-connected frameworks, but other polyhedra types may also be incorporated into microporous structures. This communication describes $Zn_4O(BO_3)_2$, a zincoborate built up from tetrahedral $ZnO_4$ and triangular $BO_3$ sub-units.

Substitution of boron for aluminum and/or silicon in zeolite molecular sieves has long been a topic of interest.[1,2,3] A rare example of complete boron substitution for both Si and Al is provided by "boralite," $Zn_4O(BO_2)_6$,[4] a direct topological analogue of the aluminosilicate sodalite-type framework, for example, $Na_4OH(AlSiO_4)_3$.[5] In general, however, boron atoms, usually substituting for aluminum atoms, have only been introduced into aluminosilicate molecular sieves in small quantities, although the technological implications of such doping reactions are extremely important, as in the boron/MFI zeolite.[6]

In this communication, we describe one result of our exploratory syntheses in the zincoborate structure field, complimenting the rapidly-growing family of zincophosphate and related (Be/Zn)(P/As) molecular sieves,[7,8] consisting of framework elements from periodic-table-groups 2, 12 and 15. $Zn_4O(BO_3)_2$ is a novel *neutral*-framework material containing micro-pores, built up from "fused", vertex-sharing tetrahedral $ZnO_4$ and triangular $BO_3$ units. Several other zincoborate compounds are known,[9] but none are similar to the phase described herein.

The final atomic coordinates for $Zn_4O(BO_3)_2$ are listed in Table II, with selected geometrical data in Table III. $Zn_4O(BO_3)_2$ has a 3-dimensional structure built up from 5 asymmetric-unit atoms (1 Zn, 1 B, 3 O), forming vertex-sharing tetrahedral $ZnO_4$ and (almost) triangular $BO_3$ building blocks, which enclose small, elongated cavities (Figure 1) and a three-dimensional network of channels (Figure 2). These channels propagate in the crystallographic [100], [010] and [001]-directions: Their estimated diameter is 3.5 Å. Each oxygen atom is bound to *three* neighbors—two zinc atoms and one boron atom for O(1) and O(2), and three zinc atoms for O(3). Average geometrical parameters are as follows: $d_{av}$(Zn–O) = 1.939 (3) Å, $d_{av}$(B–O) = 1.412 (4) Å, $\theta_{av}$(O–Zn–O) = 109.5 (2)° and $\theta_{av}$(O–B–O) = 120.0 (4)°. The Zn/B/O connectivity in $Zn_4O(BO_3)_2$ leads to the presence of oxygen-bridged "3-rings" (Figure 3) and "5-rings" of nodal (Zn and B) atoms surround-

ing the central cage, although the oxygen atoms in these rings are all 3-coordinate as noted above, compared to the typical 2-fold $T$–O–$T'$ connectivity in tetrahedral molecular sieve structures. The atomic-connectivity in these "fused" rings is: $\overline{\llcorner \mathrm{Zn}-\mathrm{B}-\mathrm{Zn} \lrcorner}$ and $\overline{\llcorner \mathrm{Zn}-\mathrm{B}-\mathrm{Zn}-\mathrm{B}-\mathrm{Zn} \lrcorner}$, respectively, ignoring oxygen atoms, *i.e.*, each ring contains a Zn–O–Zn linkage, but no B–O–B links. Extending *Smith's* zeolite-cage nomenclature scheme[18] to this new type of connectivity would result in an 18-nodal-atom cage with the designation $3^6 5^4$ (six 3-rings and four 5-rings). These cages are aligned in the crystallographic [111]-direction, and interlinked resulting in a three-dimensional microporous network.

In summary, we have prepared and characterized a new, neutral-framework, zincoborate structure containing a novel network of small channels and cavities. Typically, a powder was produced, but the crystal structure was elucidated by *ab initio* methods from laboratory X-ray data, indicating the power of current diffraction software techniques. Further synthetic work is now in progress to determine if other novel, open, structures containing triangular boron atoms as framework species can be prepared. The presence of oxygen-atom vacancies in the framework is also notable, and may facilitate substitution reactions with the Zn/B/O framework itself.

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**Experimental Procedure:**

*Synthesis*: The hydrothermal reaction (sealed TEFLON pouch, 200 °C, 4 days, pH $\approx$ 8.5) of 3.814 g of borax ($Na_2B_4O_7 \cdot 10H_2O$), 3.440 g of 4 M NaOH solution, 6.43 g of $Zn(NO_3)_2$ and 10 $cm^3$ of water resulted in a highly-crystalline white powder, which could be indexed "by hand" on a rhombohedral basis, with approximate lattice constants of $a = 9.910$ Å and $\alpha = 48.62°$ (hexagonal setting: $a \approx 8.160$ Å, $c \approx 26.156$ Å). The systematic absences of the powder data (rhombic setting: $hhl$, $l = 2n$; $hhh$, $h = 2n$) indicated space groups $R3c$

or $R\bar{3}c$, and no "extra" lines were left un-indexed. A powder-second-harmonic-generation (PSHG) test[10] gave a null response, indicating that the material probably crystalizes in a centrosymmetric space group. Space group $R\bar{3}c$ (No. 167) w s hereafter assumed for this material, and confirmed by the successful course of the structure refinement. Thermogravimetric analysis indicated no weight loss for this material below 600 °C.

*Structure Determination*: The crystal structure of $Zn_4O(BO_3)_2$ was solved *ab initio* from laboratory X-ray powder data.[11,12,13] High-resolution data were collected for a flat-plate sample of $Zn_4O(BO_3)_2$ over a 12 hour period on a Scintag PAD-X automated diffractometer operating in $\theta$-$\theta$ geometry between $2\theta = 16$ and $100\,°$, with a step-size of $0.02\,°$. Optimal estimates of the individual reflection intensities were extracted by a profile-fitting method invented by Pawley[14] and developed by Le Bail.[15] The appropriate "profile" parameters were refined by least-squares fitting and the intensities themselves (with respect to the Cu $K\alpha_1$ wavelength) were optimized by an "iterative" procedure[15] using the program GSAS.[16] A total of 186 structure-factor-moduli ($F_{hkl} > 0$), corrected for Lorentz, polarization, and multiplicity effects were obtained from the data, compared to a maximum possible number of ~230 $F_{hkl}$ values observable to that $(\sin\theta)/\lambda$ limit. These $F_{hkl}$-values were used to develop a direct methods solution (software: SHELXS-86;[17] 335 triplet-phase-relations, 7 negative-quartet-phase-relations generated) for the crystal structure of $Zn_4O(BO_3)_2$. Careful examination of the direct methods results indicated a plausible tetrahedral fragment [eventually atoms Zn(1) and O(1)], and the odel was developed further by geometrical placement of the 2 remaining tetrahedral vertices about the center of this fragment, assuming reasonable Zn–O bond distance/angle parameters. These two $ZnO_4$ vertices [O(2) and O(3)] were both evidently on crystallographic special positions (see Table II) and were constrained as such. These four atomic positions were used as the starting model for a conventional Rietveld refinement against the X-ray powder data.

The Rietveld refinement (program: GSAS) progressed smoothly and profile and atomic parameters were progressively added to the model as variables in the normal way. A 5-parameter pseudo-Voigt function was used to describe the X-ray line-shape and its width variation with scattering angle, and a correction for preferred orientation (direction <111>) was allowed to vary during the refinement. At the end of the initial refinement, a difference Fourier synthesis identified one distinct peak at $\sim (0.74, 0.75, \frac{1}{4})$ which was a chemically-reasonable site for a boron atom to occupy. Bond-distance restraints were applied to this B-atom site ($d$(B–O) = 1.43(2) Å) to assure a stable convergence of the boron-atom positional parameters. Assuming full occupancy for all five atom sites results in a unit-cell stoichiometry of $Zn_{12}B_6O_{22}$ which does not charge-balance (apparent charge = −2). Because no extra-framework sites were apparent from Fourier maps, the oxygen fractional occupancy factors were refined. Those for O(1) and O(3) refined to values near to unity (1.00 (2) and 1.08 (3) respectively), while that of O(2) refined to a value of 0.84 (2). The fractional occupancy of O(2) was then fixed at 0.833, and those for O(1) and O(3) were set to 1.0, giving a charge-neutral unit-cell content of $Zn_{12}B_6O_{21}$, or $Zn_4O(BO_3)_2$. Refining this model resulted in a satisfactory convergence to final agreement values of $R_p$ = 10.9% and $R_{wp}$ = 14.2%, as defined in Table I. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-W-7514 Eggenstein-Leopoldshafen 2 (FRG) on quoting the depository number CSD-_____, the names of the authors and the journal citation.

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## Figure Captions

Fig. 1. ORTEP plot of the cage configuration in $Zn_4O(BO_3)_2$, viewed perpendicular to the [111]-cage axis, showing the fused 3- and 5-ring linkages: B represented by small plain circles, Zn by medium "filled" circles, O by large plain circles. Atom radii are arbitrary.

Fig. 2. ORTEP plot of the unit-cell of $Zn_4O(BO_3)_2$, viewed down the [100]-direction, showing the one-dimensional channels. B represented by small plain circles, Zn by medium "filled" circles, O by large plain circles. Atom radii are arbitrary.

Fig. 3. Detail of the 3-ring linkage in $Zn_4O(BO_3)_2$, built up from tetrahedral $ZnO_4$ and triangular $BO_3$ groups. Selected bond lengths [Å], with e.s.d.s in parentheses: Zn(1)–O(1) 1.906(5), Zn(1)–O(1)′ 1.926(5), Zn(1)–O(2) 1.962(5), B(1)–O(1) 1.435(5), B(1)–O(2) 1.367(7).

## Table I: Crystallographic Parameters

$Zn_4O(BO_3)_2$

| | |
|---|---|
| empirical formula | $Zn_4O_7B_2$ |
| formula wt. | 384.37 |
| crystal form | white powder |
| crystal system | rhombohedral |
| $a = b = c$ (Å) | 9.9115 (4) |
| $\alpha = \beta = \gamma$ (°) | 48.602 (1) |
| $V$ (Å$^3$) | 502.61 |
| $Z$ | 3 |
| space group | $R\bar{3}c$ (No. 167) |
| $T$ (°C) | 25 (1) |
| $\lambda$(Cu K$\alpha$) (Å) | 1.54178 |
| $\rho_{calc}$ (g/cm$^3$) | 3.81 |
| refinement method | X-ray Rietveld refinement |
| software | GSAS suite |
| extinction correction | none applied |
| absorption correction | none applied |
| data range | $16 \leq 2\theta \leq 100°$ |
| number of data | 4198 powder data points |
| parameters (reflections) | 31 (191) |
| $R_p(\%)^a$ | 10.9 |
| $R_{wp}(\%)^b$ | 14.2 |

$^aR_p = \Sigma\,|y_o - Cy_c|/\Sigma\,|y_o|$, $^bR_{wp} = [\Sigma\, w(y_o - C\, y_c)^2/\Sigma w {y_o}^2]^{1/2}$, where C is a scale factor.

**Table II: Structural Data**

$Zn_4O(BO_3)_2$

Rhombohedral, $R\bar{3}c$, $a = 9.9115(4)$ Å, $\alpha = 48.602(1)°$

| Atom | W* | $x$ | $y$ | $z$ | $U_{iso}$(Å$^2$) |
|---|---|---|---|---|---|
| Zn(1) | 12*f* | 0.6408 (2) | 0.6925 (2) | 0.0794 (2) | 0.007 (1) |
| B(1) | 6*e* | 0.728 (2) | 0.772 | 1/4 | 0.005† |
| O(1) | 12*f* | 0.5854 (8) | 0.8045 (7) | 0.2181 (8) | 0.007 (2) |
| O(2)§ | 6*e* | 0.396 (2) | 3/4 | 0.104 | 0.018 (4) |
| O(3) | 4*c* | 0.7986 (4) | 0.7986 | 0.7986 | 0.013 (4) |

* *W* Wyckoff-site notation, § fractional site occupancy = 5/6, †not refined

## Table III: Selected Geometrical Data

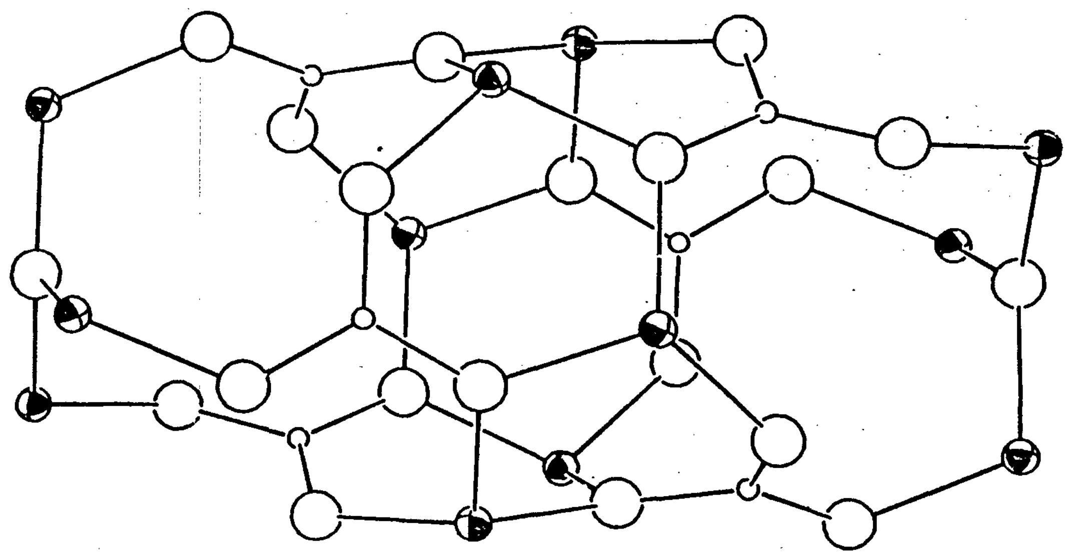
Bond distances ( Å)

| | | | |
|---|---|---|---|
| Zn(1)–O(1) | 1.906 (5) | Zn(1)–O(1)′ | 1.926 (5) |
| Zn(1)–O(2) | 1.962 (5) | Zn(1)–O(3) | 1.962 (2) |
| B(1)–O(1) × 2 | 1.435 (5) | B(1)–O(2) | 1.367 (7) |

Bond angles ( °)

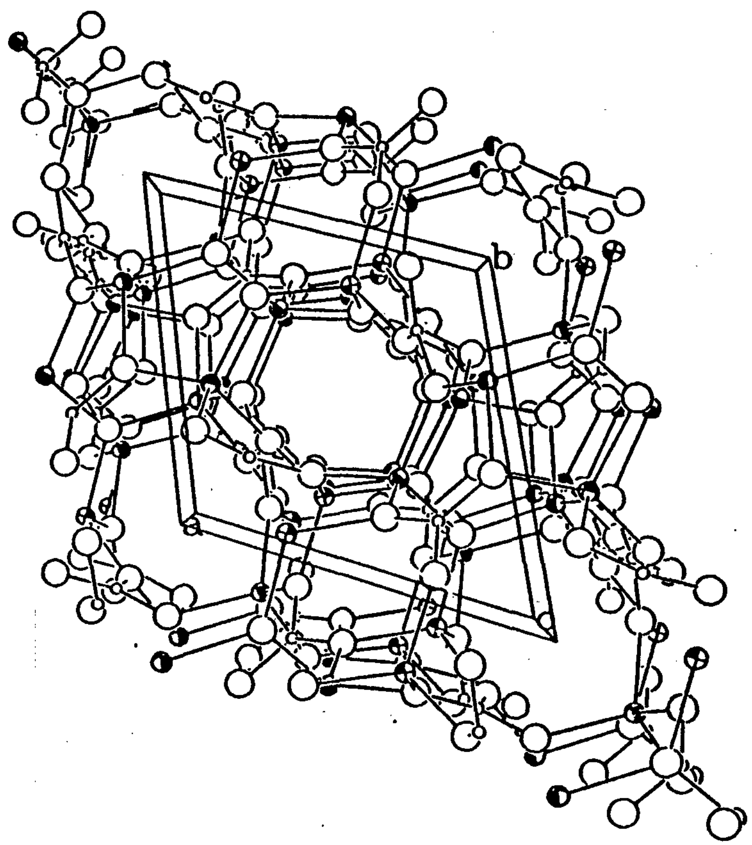
| | | | |
|---|---|---|---|
| O(1)–Zn(1)–O(1)′ | 106.2 (3) | O(1)–Zn(1)–O(2) | 110.1 (3) |
| O(1)–Zn(1)–O(3) | 112.1 (4) | O(1)′–Zn(1)–O(2) | 111.2 (2) |
| O(1)′–Zn(1)–O(3) | 110.2 (2) | O(2)–Zn(1)–O(3) | 107.2 (3) |
| O(1)–B(1)–O(1)′ | 120.1 (8) | O(1)–B(1)–O(2) | 120.0 (4) |
| O(1)′–B(1)–O(2) | 119.9 (4) | | |

the "prime" symbol indicates a crystallographically-distinct atom

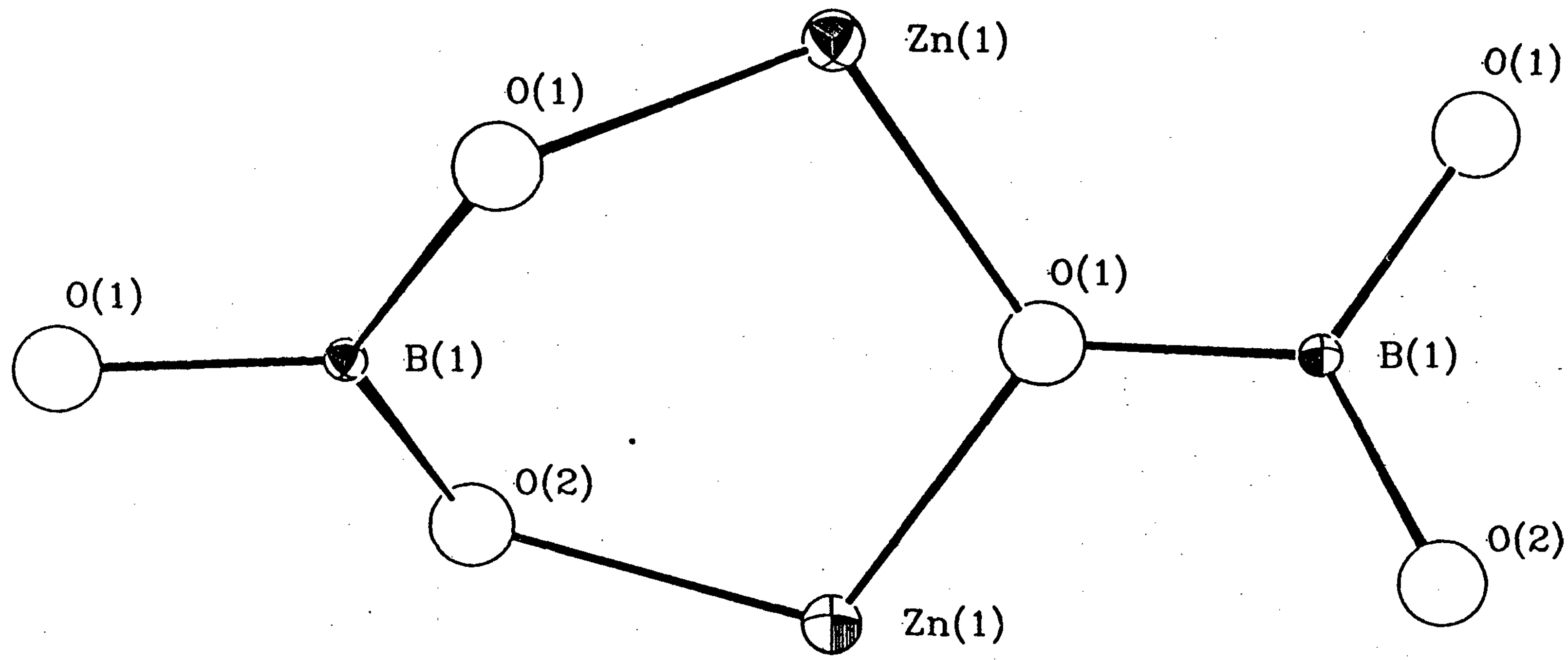


$Zn_4O(BO_3)_2$

Fig #2




$Zn_4O(BO_3)_2$




$Zn_4O(BO_3)_2$

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